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## MANY-ELECTRON THEORY OF ATOMS AND MOLECULES

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Orbital theories of atoms and molecules work quite well in a qualitative or semi-empirical way but fail when put to a quantitative test. The error, which is so large that often even molecule formation is not predicted, is generally attributed to electron correlation. Its importance has been stressed in several reviews.<sup>1, 2</sup>

Since electrons affect one another through their instantaneous potentials and not just by their average potentials as in the Hartree-Fock method,<sup>1</sup> we do have a many-electron problem. But what sort of a many-body problem? Does the long range of coulomb repulsions cause all electrons to be involved in one complicated motion? If this were the case to the extent of overcoming the effects of the exclusion principle, shell structure would be wiped out, and an atom or molecule would be more like a drop of electron liquid. Actual shell structure and electron densities are close to those given by the Hartree-Fock method. For example, densities from the latter agree quite well with X-ray results.<sup>3</sup>

The situation of the many-electron problem in atoms and molecules is compared with related many-body problems in Figure 1. Inside nuclei, strong, short-range forces cause only local nucleon pair correlations to dominate. Brueckner theory<sup>4</sup> considers these for the idealized infinite nuclear "matter." Due to the strength of repulsions, each particle moves in an environment it is constantly polarizing. In finite systems,<sup>5</sup> difficulties arise. This "polarized sea" potential is strongly dependent on particle state, so that orthogonal ground-state orbitals cannot be obtained easily. The basis is discrete, and the difficulties of evaluating slowly convergent infinite sums as in ordinary perturbation theory<sup>1</sup> appear.

In the infinite electron gas, Hartree-Fock orbitals being plane waves, there is no electron localization. As we shall see below, correlation is determined by the difference of the instantaneous coulomb potential  $g_{ij} = r_{ij}^{-1}$  between two electrons  $i, j$  and the average, i.e., Hartree-Fock (H.F.), potential they would exert on one

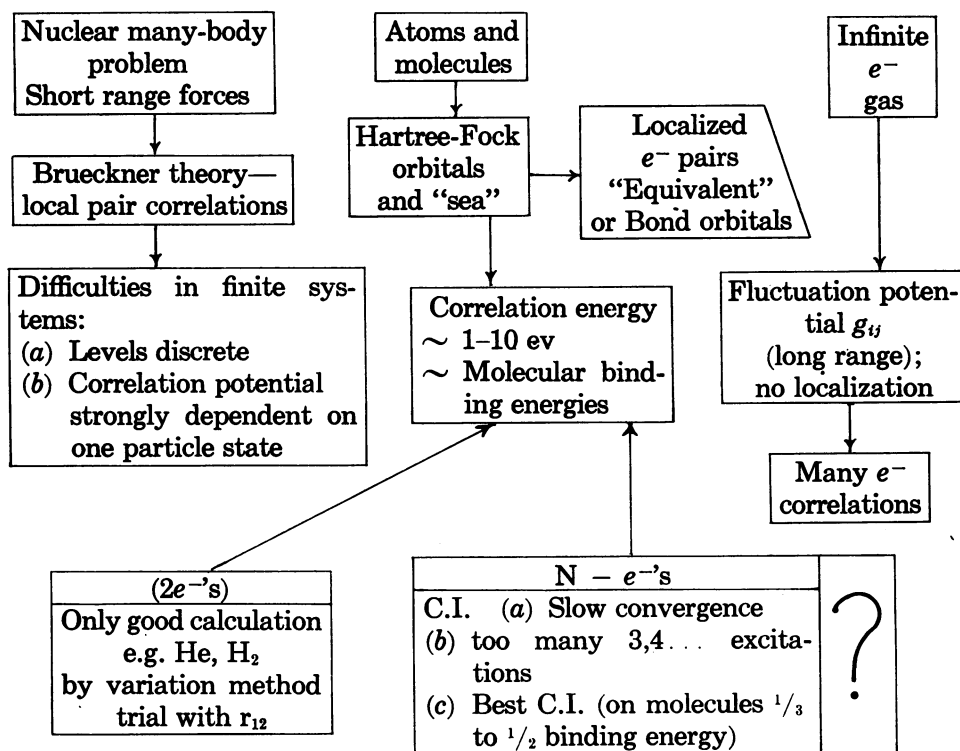


FIG. 1.—The situation of the many-electron problem in atoms and molecules and related many-body problems.

another. But due to complete delocalization, this H.F. part,  $\bar{S}_i(j) + \bar{S}_j(i)$  is uniform and nearly zero for a very large box, and the fluctuation potential is the full  $g_{ij}$  with its long range. Thus *many* electrons correlate at the same time.

Fortunately, in atoms and molecules (except dyes, etc., where metallic behavior is approached), the problem is very different from that of the electron gas. The symmetry, the nuclear wells, and the exclusion principle localize electrons with paired spins in the Hartree-Fock wave function. As shown by Linnett and Pöe,<sup>6</sup> the configuration of maximum probability given by a determinantal function, e.g., for Ne, is four electron pairs tetrahedrally arranged. Such spatial arrangements, bonds, etc., are better represented by transforming the H.F. orbitals to "equivalent orbitals" which leave the determinant unchanged.<sup>7</sup>

The only accurate calculations on atoms and molecules so far<sup>8</sup> are still those on two-electron systems based on the classical works<sup>1</sup> of Hylleraas on He, and James and Coolidge on H<sub>2</sub> using trial functions containing  $r_{12}$ . This method not having been extended to the case of  $N$  electrons, for such systems configuration-interaction (C.I.) is used. The latter is often slowly convergent (except when used for degeneracy or "resonance"), the number of multiple excitations increases very rapidly with  $N$ , and best C.I. on small molecules so far has given only about  $1/3$  to  $1/2$  of the binding energies.

We have developed an extensive theory for the  $N$ -electron atom or molecule (a) to get a quantitative scheme of the order of the difficulty of the He, H<sub>2</sub> case, (b)

to understand the physical behavior of many-electron motion and to relate the "chemical" picture to correlation. In our initial work, rigorous solutions were obtained in perturbation theory.<sup>9</sup> We have now gone far beyond those results and completed the picture in several directions. In this communication, we summarize our latest findings with emphasis on the physical basis and the over-all structure that emerges. The full mathematical theory will be published in the *Journal of Chemical Physics*.

*Physical Aspects of Correlation in Atoms and Molecules.*—The principal features of the many-electron problem in atoms and molecules are shown in Figure 2. The

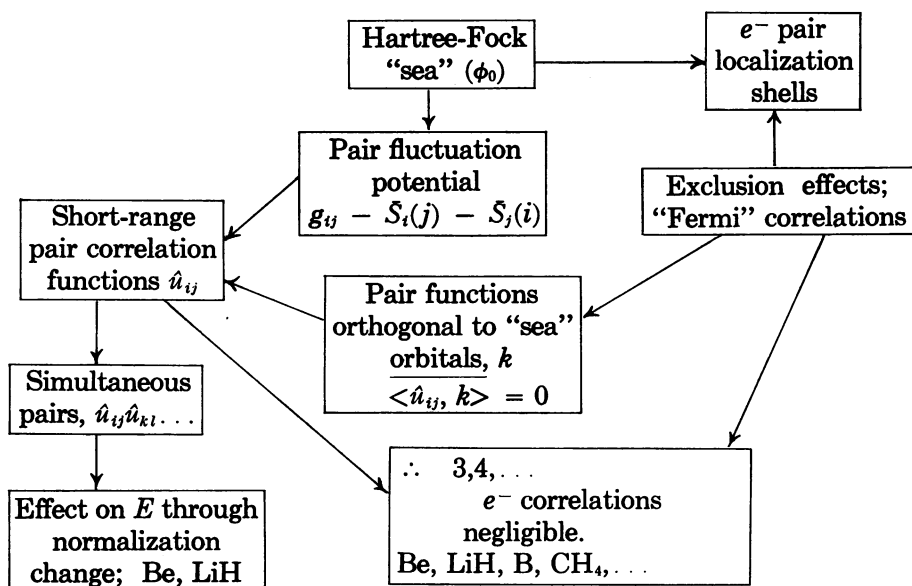


FIG. 2.—Main physical aspects of electron correlation in atoms and in molecules with no strong delocalization.

long-range effects of coulomb repulsions are well taken care of by the Hartree-Fock potential and orbitals. We start with the Hartree-Fock solution,  $\phi_0$ . The reason for the choice of this "sea" in which electrons move will become more and more apparent as we go along. The effects of using a polarized "sea" as in the Brueckner method would come up only to quite high orders and would be negligible aside from the cumbersome self-consistency procedures<sup>4, 5</sup> that it would require.

If we write 
$$\psi = \phi_0 + \chi \quad (1)$$

for the exact wave function with  $\phi_0$  the single H.F. determinant and  $\chi$  the correction for correlation, the energy is separated into an H.F. and a correlation part.

$$E = \frac{\langle \chi, H\psi \rangle}{\langle \chi, \chi \rangle} = E_{\text{H.F.}} + \frac{2 \langle \phi_0, (H - E_{\text{H.F.}})\chi \rangle + \langle \chi, (H - E_{\text{H.F.}})\chi \rangle}{1 + 2 \langle \phi_0, \chi \rangle + \langle \chi, \chi \rangle} \quad (2)$$

$$E_{\text{H.F.}} = \langle \phi_0, H\phi_0 \rangle,$$

and

$$H = \sum_{i=1}^N h_i^0 + \sum_{i>j} g_{ij} = H_0 + H_1, \quad (3)$$

with  $h_i^0$  the bare nuclei hamiltonian of electron  $i$  and  $g_{ij} \equiv 1/r_{ij}$ . We separate  $H$  into a

$$H_0 = \sum_{i=1}^N (h_i^0 + V_i) \quad (4)$$

part for independent electrons in the H.F. potential  $V_i$  and a residual "fluctuation" potential part

$$H_1 = \sum_{i>j}^N [g_{ij} - \bar{S}_i(j) - \bar{S}_j(i)], \quad (5)$$

writing<sup>9</sup>  $\sum_{i=1}^N V_i$  as  $\sum_{i>j}^N [\bar{S}_i(j) + \bar{S}_j(i)]$ . An  $\bar{S}_i(j)$  is the coulomb plus exchange potential of orbital  $i$  acting on electron  $j$ . Then

$$E_{\text{H.F.}} = E_0 + E_1 = \sum_{i=1}^N \epsilon_i - \sum_{i>j}^N (J_{ij} - K_{ij}) \quad (6)$$

with  $\epsilon_i$  the H.F. orbital energies,  $J_{ij}$ ,  $K_{ij}$  the coulomb and exchange integrals.  $(H - E_{\text{H.F.}})$  becomes

$$(H - E_{\text{H.F.}}) = \sum_{i=1}^N e_i + \sum_{i>j} m_{ij}, \quad (7a)$$

where

$$e_i \equiv h_i^0 + V_i - \epsilon_i$$

and

$$m_{ij} = g_{ij} - \bar{S}_i(j) - \bar{S}_j(i) + J_{ij} - K_{ij}. \quad (7b)$$

A Hartree-Fock spinorbital occupied by electron  $i$  before antisymmetrization is denoted by  $i$  also, so that

$$e_i i = 0 \quad \text{from} \quad H_0 \phi_0 = E_0 \phi_0.$$

Equation (2) becomes

$$E - E_{\text{H.F.}} = \frac{2 \langle \phi_0, \sum_{i>j} m_{ij} \chi \rangle + \langle \chi, (\sum_{j>j} e_i + \sum_i m_{ij}) \chi \rangle}{1 + 2 \langle \phi_0, \chi \rangle + \langle \chi, \chi \rangle}. \quad (8)$$

*Fluctuation Potential.*—Correlation behavior is determined (a) by the pairwise fluctuation potentials  $m_{ij}$ , and (b) by the electron distribution in the "sea,"  $\phi_0$ , which depends strongly on its antisymmetric character.<sup>6, 7</sup>

An  $m_{ij}$  is usually of short range in directions going from orbital to orbital. Take a (1s) electron and another in the *Be* atom for example. An electron placed at  $r_2$  sees the average coulomb potential  $S_1(r_2)$  of the (1s) electron with opposite spin as shown in Figure 3 (taking a Slater (1s) orbital with exponent 3.70 as sufficiently close to H.F.). The (1s) electron is most likely to be found at  $r_1 = 0.27$  a.u. (Bohr orbit in *Be*<sup>+2</sup>). If it were there instantaneously, electron two would see the  $g_{12} = r_{12}^{-1}$ , also shown in Figure 3.

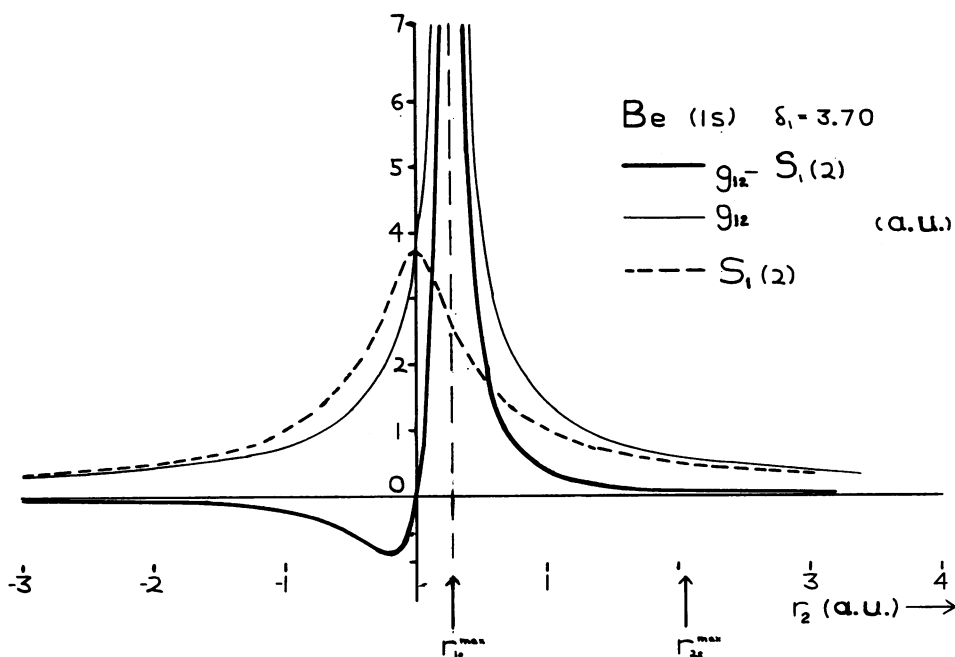


FIG. 3.—Fluctuation potential ( $g_{12} - S_1(2)$ ) as seen by an electron at  $r_2$  due a (1s) electron with opposite spin instantaneously at its Bohr radius and in line with  $r_2$ . Note that this potential which determines the correlation, is of short range through  $g_{12} = r_{12}^{-1}$  and the Hartree-Fock potential,  $S_1(2)$ , are long range.

The difference,  $g_{12} - S_1(2)$ , differing from  $m_{12}$  by the constant value 0.39 a.u., is the fluctuation potential, which shows where electron two ( $r_2$ ) would want to be if electron one were at  $r_{1s}^{\max} = 0.27$  a.u. Both  $g_{12}$  and  $S_1(2)$  are of long range, but  $m_{12}$  has a short range. It has died off before reaching a distance of 2.1 a.u., about the Bohr radius of (2s) in Be. The singularity of  $g_{12}$  at  $r_{12} = 0$  is the main feature left in  $m_{12}$ . Note also the minimum in  $m_{12}$  on the other side of the nucleus. Similar curves and surfaces can be drawn by varying  $r_1$  and  $\theta_{12}$  (angle between  $r_1$  and  $r_2$ ) also. These would aid the selection of trial functions to give maximum charge density at the dips and zero at singularity.

The exclusion principle, by putting the third and fourth electrons in a different shell, keeps them at a safe distance from the fluctuation potentials of the (1s)<sup>2</sup> electrons. As the discussion of other cases below will show, this phenomenon is quite general and even in more subtle cases leads to local pair correlations as the main effects, making the "collisions" of three, four, . . . electrons usually negligible.

This fact manifests itself in the equation:

$$\chi \sim \chi_s = \sum_{i>j}^N \frac{\alpha}{\sqrt{2}} \left( 1, 2, 3 \dots N \frac{\hat{u}_{ij}}{ij} \right) \quad (9)$$

where 1, 2, . . .  $N$  are the spin-orbitals in  $\phi_0$  occupied by electrons with the same numerals before the antisymmetrizer  $\alpha$  makes them indistinguishable. The  $\hat{u}_{ij}$  is the antisymmetric correlation wave function of  $i$  and  $j$  which shows how they are thrown out of each other's way by  $m_{ij}$ . In the orbital representation,  $\hat{u}_{ij}$  contains all double excitations of orbitals  $i, j$  from the "sea,"  $\phi_0$ . The two electrons cannot

go into regions already occupied by other electrons, and this effect of the exclusion principle is reflected in the orthogonality<sup>9</sup> of  $\hat{u}_{ij}$  to the orbitals of  $\phi_0$ , i.e.

$$\langle \hat{u}_{ij}(x_i, x_{xj}), k(x_i) \rangle_{x_i} = 0 \quad (k = 1, 2, \dots, N) \quad (10)$$

where integration is performed over  $x_i$  only. The  $\hat{u}_{ij}$  does not contain any single excitations either<sup>9</sup> ( $k = i$  or  $j$ ), because any further adjustment of the orbitals in the "sea" (Brueckner method) is negligible. The major adjustment has been done already in the Hartree-Fock method.

Equations (9) and (10) come out exactly<sup>9</sup> in first-order perturbation  $\chi_1$  beyond H.F., i.e., if only part of the energy, equation (8), is minimized.<sup>10</sup> Then  $\hat{u}_{ij}$  would be the solution,  $\hat{u}_{ij}^{(1)}$ , of the first-order part of the Schrödinger equation<sup>11</sup> of two electrons in the H.F. "sea":

$$(e_i + e_j)\hat{u}_{ij}^{(1)} + \hat{m}_{ij}\mathcal{B}(ij) = 0. \quad (11)$$

$\mathcal{B}$  antisymmetrizes  $i$  and  $j$ . The  $(\hat{m}_{ij}\mathcal{B}ij)$  is  $m_{ij}\mathcal{B}(ij)$  made orthogonal to all  $k$  as in equation (10); thus  $\hat{m}_{ij}$  is even more localized than  $m_{ij}$ .

We shall now leave equations (9) and (10) quite general and not confine  $\hat{u}_{ij}$  to any order of approximation. Various ways of obtaining the pair correlations exactly will be discussed later.

*Unlinked Clusters versus Many-Electron Correlations.*—The complete  $\chi$  would contain in addition to equation (9), "clusters" of three, four, etc., electrons at a time ( $\hat{U}_{123}$ ,  $\hat{U}_{1234}$ , etc.). In addition to these terms, just the substitution of  $\chi_s$ , equation (9), into the energy, equation (8), introduces three-electron correlations. The analysis is carried out easily with diagrams giving the energy of  $\chi_s$  as

$$E_s - E_{\text{H.F.}} \leq \frac{1}{D} \left( \sum_{i>j} \bar{\epsilon}_{ij} + 4 \sum_{ijk} \begin{array}{c} i \quad j \\ \circ \quad \circ \\ \diagdown \quad \diagup \\ \circ \quad \circ \\ \quad \quad \circ_k \end{array} \right) \quad (12)$$

$$\bar{\epsilon}_{ij} = 2 \langle \mathcal{B}(ij), m_{ij} \hat{u}_{ij} \rangle + \langle \hat{u}_{ij}, (e_i + e_j + m_{ij}) \hat{u}_{ij} \rangle \quad (13)$$

$$D = 1 + \langle \chi_s, \chi_s \rangle = 1 + \sum_{i>j} \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle \quad (14)$$

The triangle is the three-electron correlation involving the product of  $\hat{u}_{kj}$ ,  $\hat{u}_{ij}$ , and  $m_{ki}$ . Because of the physical effects described,  $\hat{u}_{kj}$  and  $\hat{u}_{ji}$  will not both be large in the same region of space, so that only pair energies in equation (12) are significant.

In the recent configuration-interaction study<sup>12</sup> of the Be atom starting with H.F., single and triple excitations were found entirely negligible. But important quadruple excitations appeared—at first sight a surprising result, since the probability of a four-electron "collision" ought to be smaller than that of a three-body one.

Equation (9) represents only two electrons correlating at one time. Actually, it is very likely that when two electrons "collide," somewhere else in the system other binary "collisions" will be taking place independently but simultaneously. To account for these, all possible products of independent pair functions must be added to  $\chi_s$ ; e.g., for Be:

$$\chi_{ss} = \frac{\alpha}{2} (\hat{u}_{12}\hat{u}_{34} + \hat{u}_{13}\hat{u}_{24} + \hat{u}_{14}\hat{u}_{23}). \quad (15)$$

As in the theory of imperfect gases, these are "unlinked clusters" and have played an important role in other many-body problems.<sup>4, 13</sup>

If in *Be*, true four-electron correlations,  $\hat{U}_{1234}$ , are negligible; the coefficients of quadruple excitations should be given only by those of double excitations. In Table 1, such coefficients from equation (15) are compared with those from the

TABLE 1  
UNLINKED CLUSTERS VERSUS FOUR-ELECTRON CORRELATIONS IN BE ATOM

Four-excited configuration	Coefficient from 37-configuration wave function*	Calc'd. [Eq. (15)] Unlinked cluster coefficient
$P_1^2(^1S)p_{11}^2(^1S)$	0.09706	0.0373
$P_1^2(^1S)s_{11}^2(^1S)$	0.03535	0.03347
$P_1^2(^1S)d_{11}^2(^1S)$	0.00159	0.00168
$P_{11}^2(^1S)d_1^2(^1S)$	0.000464	0.000478
Energy contribution	-0.075 ev	-0.074 ev

\* From Watson.<sup>12</sup>

37 configuration<sup>12</sup> C.I. The agreement is indeed satisfactory. We have obtained similar results upon examining recent C.I. results<sup>14</sup> on *LiH*.

*Effect on Energy.*—The energy effect of unlinked clusters such as in Equation (15), is again analyzed with diagrams. One gets from equation (8).

$$E - E_{H.F.} \leq \sum_{i>j}^N \tilde{\epsilon}_{ij} \frac{D_{ij}}{D'} + \frac{R}{D'} \quad (16a)$$

$D' \cong D$  and  $R$  contains all triangles, squares, and other joint four- or more-electron correlation effects.

$$D_{ij} = 1 + \sum_{k,l \neq i,j} < \hat{u}_{kl}, \hat{u}_{kl} > + \dots \quad (16b)$$

As  $N$  tends to infinity,  $D_{ij}/D$  approaches 1.<sup>4, 13</sup> In atoms and molecules if  $D$  is sufficiently different from unity due to some "resonance" as in *Be* (large  $2s^2 - 2p^2$  mixing which makes *Be* a metal not an inert gas), unlinked clusters affect the energy by canceling part of  $D'$ . This energy change agrees perfectly with the 37 C.I. result in Table 1, showing also that  $R$  in equation (16a) is negligible as anticipated. Thus,

$$E - E_{H.F.} \cong \sum_{i>j} \tilde{\epsilon}_{ij} D_{ij}/D. \quad (17)$$

One reason for the smallness of many-particle effects is the smallness of  $\hat{u}_{ij}$ . Even with the  $2s^2 - 2p^2$  "resonance" in *Be*,  $D$  gets only as large as 1.09. Usually  $D \cong D_{ij} \cong 1$ . Equation (17) will usually be a good approximation, but if need be, the neglected terms,  $R$ , can also be estimated with  $\hat{u}_{ij}$  and an upper limit obtained to  $E$ .

*Exclusion effect in boron.*—We have seen how and why three-, four-, and more-electron correlations become unimportant when electrons are localized in radially different regions of space as in *Be* and *LiH*. What about cases, however, which involve say  $2s$ ,  $2p$  electrons which are radially all in the same vicinity?

To see how three-electron correlations are expected to behave in such cases, we examine the boron atom. Almost all of the  $(2s)^2$  correlation,  $\hat{u}_{34}$ , in *Be* is due to  $(2p)^2$  mixing.<sup>12</sup> There,  $\hat{u}_{34}$  is  $^1S$ , a combination of three  $(2p)^2$  determinants. When

a  $(2p_z\alpha)$ , i.e., spinorbital 5, is put on top of the  $(2s)^2$  shell as in boron however,  $\hat{u}_{34}$  becomes orthogonal to it, i.e.  $\langle \hat{u}_{34}, 5 \rangle = 0$ . Instead of the whole sphere,  $\hat{u}_{34}$  will now be large only on the  $xy$ -plane as shown in Figure 4. To make the three-electron  $(2s_\alpha 2s_\beta 2p_z\alpha \equiv 345)$  correlation, i.e., the triangle of equation (12), appreciable, the product  $\hat{u}_{34}\hat{u}_{45}$  must be large. But  $\hat{u}_{45}$  is large where its fluctuation potential  $m_{45}$  and  $B(45)$  are large [see equation (11)]. The fluctuation potential,  $(g_{45} - S_5(4))$ , that electron 4 sees when 5 is at its most likely place (Fig. 4) is shown

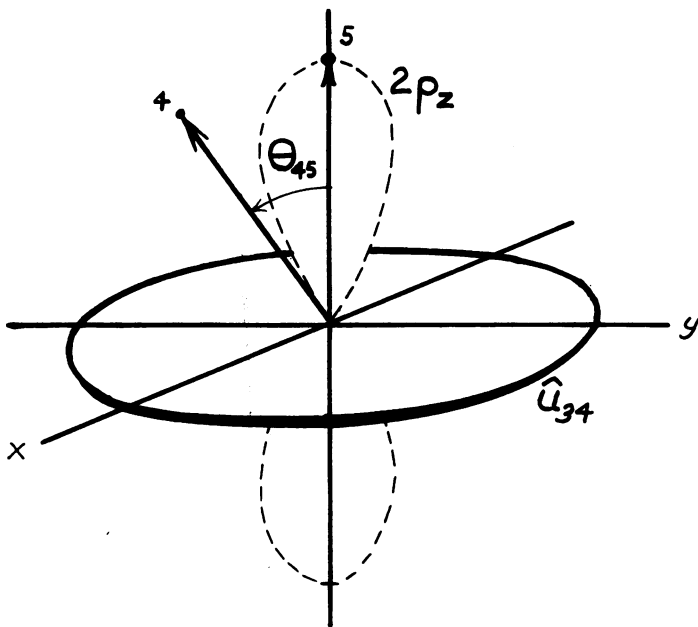


FIG. 4.—Exclusion effect in Boron ( $1s^2 2s^2 2p_z$ ). The two  $(2s)$  electrons while correlating are kept away from the  $(2p_z)$  electron which has the same spin as one or the other  $(2s)$ . Thus  $(2s)^2$  correlation,  $\hat{u}_{34}$ , is confined to the vicinity of the  $xy$ -plane.

in Figure 5 for a fixed radius.

Note that  $m_{45}$ , hence  $\hat{u}_{45}$ , is very small just where ( $\sim 90^\circ$ )  $\hat{u}_{34}$  is large. Thus, the product  $\hat{u}_{34}\hat{u}_{45}$  will be small everywhere, again exhibiting the combined behavior of  $m_{ij}$  and exclusion to make many-electron correlations unimportant.

*How to Get the Pair Functions.*—Having a sum of pair energies in equation (17), each pair function can be obtained separately in several ways, depending on the magnitude of  $(D_{ij}/D)$ . These ways and the over-all picture that comes out of our theory is shown in Figure 6.

Each  $\bar{\epsilon}_{ij}$ , equation (13), varied subject to orbital orthogonality, equation (10), yields Schrödinger equations of electron pairs in a Hartree-Fock “sea.”

$$(e_i + e_j + \hat{m}_{ij})\phi_{ij} = 0 \quad (18a)$$

where  $\phi_{ij} = \mathcal{B}(ij) + \hat{u}_{ij}$ . When this equation is satisfied,  $\bar{\epsilon}_{ij}$  becomes

$$\epsilon_{ij} = \langle \mathcal{B}(ij), g_{ij}\hat{u}_{ij} \rangle. \quad (18b)$$

Minimization of smaller parts<sup>10</sup> of  $\bar{\epsilon}_{ij}D_{ij}/D$  leads to first-order pairs,<sup>9</sup> equation (11). On the other hand, a more complete Schrödinger equation than equation



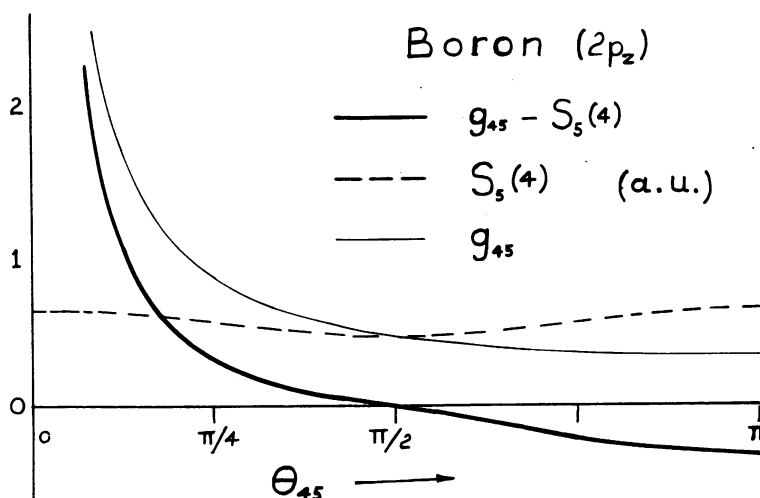


FIG. 5.—Reason for expecting  $(2s)^2(2p_z)$  three  $e^-$  correlation to be small. The fluctuation potential,  $[g_{45}-S_5(4)]$ , seen by the  $(2s)$  electron, 4, due to electron 5 at the maximum of  $(2p_z)$  is *ca.* zero on the  $xy$ -plane ( $\pi/2$ ) where  $u_{34}$  was largest (Fig. 4).

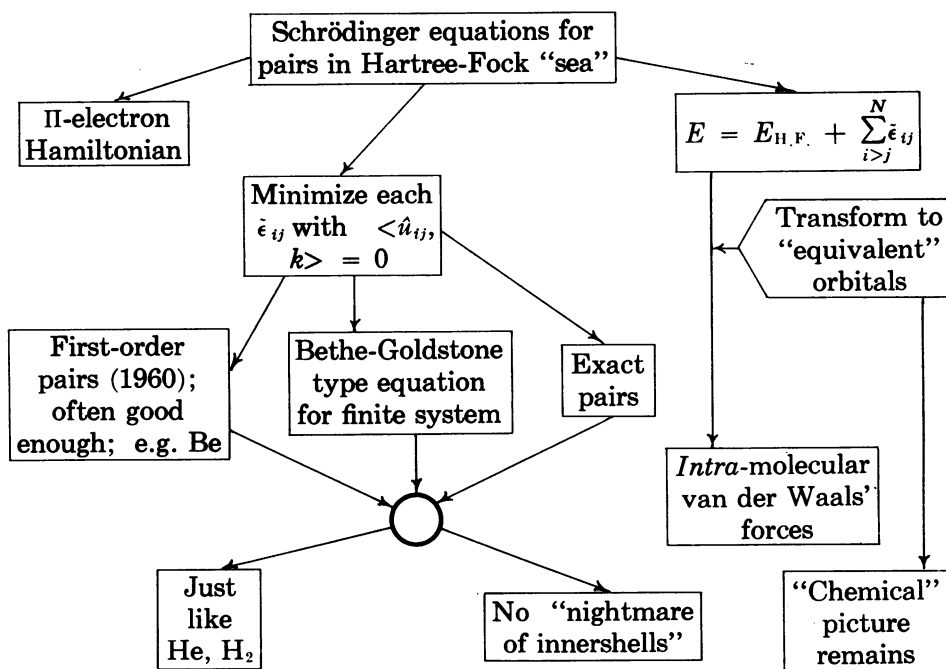


FIG. 6.—Principle features and ways of using the many-electron theory of atoms and molecules as reported in text.

(18a) is obtained by minimizing  $\epsilon_{ij}/(1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle)$  instead of  $\epsilon_{ij}$  alone. Equation (18a) differs from the closed form of the Bethe-Goldstone<sup>15</sup>–Brueckner equation in containing  $\hat{m}_{ij}$  instead of  $\hat{g}_{ij}$ . The results we have obtained in this connection should also be useful for finite nuclei.

Now the variational *minimum* principle can be applied to each  $\epsilon_{ij}$ , equation (13), separately subject to equation (10) and with trial functions that may contain  $r_{12}$  explicitly as in *He* and *H<sub>2</sub>* for shells with a strong "correlation hole."<sup>1</sup> For others, e.g., those with "resonance" as in the  $(2s)^2$  of *Be*, a small secular equation need be solved mixing a few configurations. The number of independent pair functions that are needed<sup>9</sup> is much smaller than  $N(N - 1)/2$  due to the multiplicity of many pair states such as  $^3S$ ,  $^1D$ , etc. Only 9 pair functions of which 6 are singlets must be obtained for *Ne*, instead of 45. Because of orbital orthogonality, equation (10), the *minimization* procedure can be applied even to outer shell pairs with no fear of converging to the wrong shell ("the nightmare of inner shells" which plagued the quantum chemistry of the thirties).<sup>16</sup>

*The "Chemical" Picture.*—Equation (18) for an outer pair with  $V_i + V_j - \bar{S}_i - \bar{S}_j = V_{\text{core}}$  (Eq. 7b) has the form of a " $\Pi$ -electron Hamiltonian" thus providing a basis for such semiempirical schemes.<sup>17</sup> Moreover,  $\epsilon_{ij}$  can be added to  $(J_{ij} - K_{ij})$ , equation (6), explaining the successes of semiempirical M.O. calculations.

In molecules with no strong electron delocalization, the Hartree-Fock orbitals in  $\phi_0$  can be transformed<sup>7</sup> into "equivalent orbitals." Then  $\sum_{i < j} \epsilon_{ij}$  becomes simply the sum of "bond" correlation energies and "Van der Waals" attractions between non-bonded regions. The latter were discussed semi-empirically by Pitzer.<sup>2</sup> One can use the theory both ways and (a) calculate such Van der Waals forces having C.I. etc. type correlation results starting with Hartree-Fock, or (b) estimate correlation energies of pairs of H.F. orbitals from estimates of bond energies and London dispersion type forces.<sup>2</sup>

Thus the "chemical" picture with its bonds, Lewis-Langmuir octets<sup>6</sup> and orbitals remains *in spite of correlation*.

It is my great pleasure to thank Raymond M. Fuoss and Lars Onsager for the kind interest they showed in this work.

<sup>1</sup> Löwdin, P. O., in *Advances in Chemical Physics* (New York: Interscience Publishers, 1959), vol. 2.

<sup>2</sup> Pitzer, K. S., in *Advances in Chemical Physics* (New York: Interscience Publishers, 1959), vol. 2.

<sup>3</sup> See, e.g., Daudel, R., R. LeFebvre, and C. Moser, *Quantum Chemistry* (New York: Interscience Publishers, 1959).

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<sup>6</sup> Linnett, J. W., and A. J. Pöe, *Trans. Faraday Soc.*, **47**, 1033 (1951).

<sup>7</sup> See e.g., Pople, J. A., *Quart. Revs. (London)*, **11**, 291 (1957).

<sup>8</sup> The next best calculation is the recent one on *Be* (reference 12). Here  $(2s)^2-(2p)^2$  "resonance" is of utmost importance and corrects for much of the correlation.

<sup>9</sup> Sinanoğlu, O., *Proc. Roy. Soc. (London)*, **A260**, 379 (1961).

<sup>10</sup> Sinanoğlu, O., *J. Chem. Phys.*, **34**, 1237 (1961).

<sup>11</sup> As shown in reference 9, for a general pair  $\mathfrak{B}(ij)$  is replaced by a pure symmetry state combination.

<sup>12</sup> Watson, R. E., *Phys. Rev.*, **119**, 170 (1960).

<sup>13</sup> Brout, R., *Phys. Rev.*, **111**, 1324 (1958).

<sup>14</sup> Ebbing, D. D., Ph.D. Thesis, Department of Chemistry, Indiana University (June 1960).

<sup>15</sup> Bethe, H. A., and J. Goldstone, *Proc. Roy. Soc. (London)*, **A238**, 551 (1956).

<sup>16</sup> Van Vleck, J. H., and A. Sherman, *Revs. Modern Phys.*, **7**, 167 (1935).

<sup>17</sup> Pariser, R., and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).